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by

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Weathering steel samples were exposed for periods of up to 30 months at nine air monitoring sites in the St. Louis, Missouri area. Climatic and air quality data were recorded during the exposure period and subjected to a rigorous evaluation to eliminate recording errors and to estimate missing values. Weight loss was used as the measure of steel corrosion. Corrosion rate was evaluated with respect to, 1) flux of pollutants (sulfur oxides, nitrogen oxides, oxidants, and particles) to the steel during both wet and dry periods, 2) temperature, and 3) exposure history. Different definitions of when the steel was wet were evaluated to determine the most likely "critical relative humidity." Non-linear multiple regression techniques were used to determine the statistical significance of each factor and develop a theoretically consistent environmental damage function.

From the fall of 1974 to the spring of 1977, EPA conducted an air pollution modeling study in St. Louis, Missouri (1). Nine of 25 continuous air monitoring sites were selected for studying the effects of pollutants on eight types of materials (2). Weathering steel was one of the materials. This paper presents the results of analyzing the corrosion of weathering steel with respect to environmental data.

Theoretical Considerations

Many metals form corrosion product films as they corrode. These films tend to restrict the rate of corrosion. In general, the rate of corrosion is inversely proportional to the thickness of the corrosion product film (rate controlled by diffusion through the film). When the film is insoluble and does not change structure with time, the corrosion-time function is parabolic ($c = \alpha\sqrt{t}$). Many metal corrosion products have solubilities that are proportional to acidity. Thus, in very acid solutions, films are very

thin and the resulting corrosion-time function is almost linear. In atmospheric exposures, there are many sets of environmental conditions where these two mechanisms are competing. The results is the empirically observed relationships, $c = At^n$, where the exponent, n, most often has a value between 0.5 and 1.0 (2-4).

Theoretically, the amount of corrosion (c) is the sum of the metal accumulated in the corrosion product film (T) and the amount of metal solubilized from that film with time (βt_w).

$$c = T + \beta t_w \tag{1}$$

where t_w is time-of-wetness and β is a solubilization rate which is a function of acidic pollutant fluxes. The rate of film thickness growth in units of metal corroded is;

$$dT/dt_w = \alpha/T - \beta \tag{2}$$

where α is a function of diffusivities through the film. Pollutants may also affect this coefficient. Under constant conditions, integration of equation (2) yields;

$$-\beta^2 t_w = \beta T + \alpha \ln(1 - \beta T/\alpha) \tag{3}$$

substituting equation (1) into equation (3) and rearranging produces the transcendental equation:

$$c = \beta t_w + \alpha(1-\exp(-\beta C/\alpha))/\beta \tag{4}$$

which is equivalent to:

$$c = \beta t_w + \alpha/(dc/dt_w) \tag{5}$$

A least squares fit of equation (4) cannot be used to determine the effects of enviornmental factors on the coefficients α and β because as α/β becomes large the equation approaches being an identity. When $\beta c/\alpha$ is large, $\exp(-\beta c/\alpha)$ approaches zero and equation (4) becomes;

$$c = \beta t_w + \alpha/\beta \tag{6}$$

At early stages of corrosion, however, from the empirically observed relationship, $dc/dt_w \simeq nc/t_w$ which yields;

$$c = \beta t_w + \alpha t_w/nc \tag{7}$$

During the first few years of corrosion of weathering steel, nearly all of the corrosion is accumulated in the film and α/nc is much greater than β, which would indicate that the corrosion-time function should be nearly parabolic. The corrosion product film on weathering steel, however, has the property that, generally, a given film thickness becomes more protective with time. An exception is when the film stays wet. In that case, the corrosion behavior of weathering steel is not much better than carbon steels. This means that n in the empirical equation At^n can be less than

0.5 and is expected to increase with fraction of time-of-wetness (f).

Measurement and Data Analysis

Environmental data. Hern, et al., (5) describes the data collection and evaluation system for the environmental parameters at the nine sites. Subsequently, the resulting Regional Air Pollution Study (RAPS) data base was revised several times using better validation techniques. The portions of that data base used in this study are hourly averages of temperature, dew point, windspeed, wind direction, total oxidant, NO_x, SO_x, and 24-hour total suspended particulate matter (TSP) samples. The validated data base contains a lot of missing hourly averages and the system was not operating during the first month or the last fifteen days in which weathering steel samples were exposed. A methodology was developed (6) to estimate these missing values using total system relationships and relationships between the system and climatological data from Lambert Field (airport meteorological station located about 16 kilometers northwest from the St. Louis central business district). Rainfall was not recorded at the exposure sites. With rainfall expected to be an important parameter, data from Lambert Field were used in this study.

Weathering Steel Corrosion. Triplicate specimens were exposed for periods varying from three to thirty months with exposures started at each of the four seasons during the first year. The experimental procedure and exposure schedule are documented in an EPA report (2). The results are 153 sets of triplicate weight loss data with site, exposure time and initial exposure season as primary variables.

Analysis of Environmental Data. Although the methodology for analyzing the data has been previously reported (6) there are some differences that should be noted. First, a later version of the RAPS data base was used as an initial sourse. Second, time-of-wetness in this paper is defined differently, thus, a relationship to calculate relative humidity from temperature and dew point is based on data for dew points greater than 0°C. Third, deposition velocities are calculated from boundary layer theory rather than empirical relationships.

This later version of RAPS data base eliminated many errors but produced more missing data.

Time-of-wetness as previously defined was the time exceeding some critical relative humidity (6). In this paper time-of-wetness is the time a critical relative humidity is exceeded and the dew point is greater than 0°C, plus any time the critical humidity is not exceeded and it is raining. For that reason a regression relating relative humidity to dew points above 0°C and temperature was used to calculate relative humidity for each hour. This relationship is:

$$RH = 100 \exp\{[-0.0722 + 0.00025(T + DP)][T-DP]\} \qquad (8)$$

where RH is relative humidity, T is temperature and DP is dew point, the later both in °C.

Deposition velocities were calculated from windspeed data. Windspeeds at tower height can be used to calculate windspeeds at specimen rack height using the relationship for rough surfaces (7):

$$V^+ = 8.5 + 2.5 \ln(Z/e) \tag{9}$$

where V^+ is the dimensionless velocity and z and e are measuring height and roughness height respectively. The rack height was about three meters from the ground. At three of the sites the meteorological towers were 10 meters while at the others they were 30 meters. The average ground roughness height was assumed to be 0.1 m. Thus, the rack height windspeed is 0.75 times the windspeed at 30 meters or 0.85 times the windspeed at 10 meters.

From anology with momentum transport, gases with a Schmidt number of approximately one that readily react at a surface, have a deposition velocity of:

$$u = V^{*2}/V \tag{10}$$

where u is the deposition velocity, V* is the friction velocity and V is the average windspeed. The friction velocity is equal to $V\sqrt{f/2}$ where f is the friction factor. From boundary layer theory for smooth flat plates (7):

$$f = 0.03/(RE_L)^{1/7} \tag{11}$$

where $RE_L = LV/\nu$, L = length of surface over which the air flows, and ν is the kinematic viscosity of air (0.15 cm^2/sec). L is assumed to be the geometric mean of the panel dimensions ($\sqrt{10.2 \times 15.2} = 12.45$ cm). Thus:

$$u = 0.35\ V_{10}^{.86} \tag{12a}$$

$$u = 0.31\ V_{30}^{.86} \tag{12b}$$

with u in cm/sec and V_{10} and V_{30} in m/sec.

Deposition velocities were calculated on an hourly basis and averaged over exposure periods. Because windspeeds are not normally distributed, the average deposition velocity is about 91% of the deposition velocity calculated from average windspeed for an exposure period.

Pollutant Fluxes. Hourly deposition velocities were multiplied by hourly pollutant concentrations to get hourly pollutant fluxes. These were summed over exposure periods for hours of wetness with different critical relative humidity criteria (75 to 90% in 5% intervals). Average fluxes were then calculated by dividing by the time-of-wetness. The results were compared with fluxes calculated by multiplying average deposition velocities for a period by the average pollutant concentration during times of wetness. The values by the two methods were fairly consistent.

Fluxes of TSP were calculated by multiplying average TSP by two-tenths of the average deposition velocity for gases (actual deposition velocities vary considerably with the size distribution of particles). Rain fluxes were calculated by dividing the amount of rain for an exposure period by time of wetness.

Statistical Analysis of Data

An initial linear regression was performed on the data to determine the relative significance of each of the factors. The form of the model was:

$$\ln(C)=\alpha_o \ln(t)+\Sigma\alpha_i \ln f_i+\beta Q+\Sigma\gamma_i P_i \qquad (13)$$

where C is amount of steel corrosion, t is total time of exposure, f is fraction of time of wetness for different critical relative humidities, Q is a temperature factor (1000[1/(273.16+T°C)-1/(273.16+T°C avg]) (6), and the P_is are the fluxes of pollutants and rain. Both forward and backward stepwise regressions were done.

The results indicated that fraction of time of wetness (f) for a critical relative humidity of 85% was the most significant of the f values, the temperature factor was somewhat less significant, and only ozone flux was not a significant factor. TSP and SO_2 had positive coefficients while the NO_2 and rain coefficients were negative.

Because the amount of corrosion of steel is expected to follow the empirical form $C = At_w^n$, where both A and n are variables with changing environmental factors, a linear regression on the ln-ln form was performed on the following model:

$$\ln(C)=\alpha_o+\alpha_1 \ln(t_w)+\alpha_2 f \ln(t_w)+\alpha_3 \ln(f)+\beta Q+ \Sigma\gamma_i P_i \qquad (14)$$

where t_w and f are time-of-wetness and fraction of time-of wetness respectively, for a critical relative humidity of 85%. The results are given in Table I.

Table I. Results of the Linear Regression of Equation:

$$\ln(C)=\alpha_o+\alpha_1 \ln(t_w)+\alpha_2 f \ln(t_w)+\alpha_3 \ln(f)+\beta Q+ \Sigma\gamma_i P_i$$

Variable	Units	Coefficient	Standard error	Partial F**
ln(C)	ln(μ)	α_o = 4.245		
$\ln(t_w)$	ln(years)	α_1 = 0.3116	0.0444	49.19
f $\ln(t_w)$	ln(years)	α_2 = 0.8583	0.1561	30.23
ln(f)		α_3 = 0.4399	0.0819	28.82
Q	*	β = -0.7023	0.1809	15.07
TSP Flux	mg/cm^2 year	γ_1 = 0.8729	0.1004	75.62
SO_2 Flux	mg/cm^2 year	γ_2 = 0.1152	0.0299	14.87
NO_2 Flux	mg/cm^2 year	γ_3 = -0.0370	0.0128	8.33
Rain Flux	cm/year	$\gamma_4 = -3.18\times10^{-4}$	1.24×10^{-4}	6.58

* Q = 1000(1/273.16+T)-1/(273.16+Tavg)) where T is in °C and Tavg is overall average of average temperatures during times-of-wetness (13.55°C).

**A measure of the statistical significance of adding the specific variable to all of the others.

The percent of variability explained by regression is 95.85%.

The fraction of time-of-wetness affects the value of n in the empirical equation $C = At_w^n$, (n=0.312+0.858f), which means that the film becomes more protective with time when f is low, but less protective with time when f is high. All of the other terms in equation 14 are considered to be a part of the A coefficient.

A pseudo steel corrosion rate was calculated by dividing steel corrosion by $f^{0.44}\ t_w^{(0.312+0.858f)}\ \exp(-0.702Q)$. This value was regressed against the pollutant and rain fluxes to determine non-exponential coefficients that make up the A term. The results are given in Table II.

Table II. Results of Regression of Pseudo Corrosion Rate Against Pollutant Fluxes

Variable	Units	Coefficient	Standard error	Partial F
Pseudo Corrosion Rate		A_0=65.63		
TSP Flux	mg/cm^2 year	A_1=85.13	9.39	82.26
SO_2 Flux	mg/cm^2 year	A_2=10.67	2.46	18.88
NO_2 Flux	mg/cm^2 year	A_3=-3.51	1.04	11.36
Rain Flux	cm/year	A_4=-0.0302	0.0085	12.51

The resulting empirical damage function, $C=At_w^n$, has the coefficients:

$$A = (65.63+85.13TSP+10.67SO_2-3.51NO_2-.03Rain)f^{0.44}\exp(-.7Q) \quad (15a)$$

$$n = 0.312+0.858f \quad (15b)$$

where the pollutant fluxes have the units in Table II. This equation accounts for 95.93 percent of the variability.

Evaluation of data with respect to theory. The significant factors in the empirical equations 15a and 15b may affect either or both α and β coefficients in equation 7. The relative effects of each parameter on α and β were determined by regressing steel corrosion/time-of-wetness (c/tw) against all of the fluxes, $1/nC_p$ (where $C_p = At_w^n$ with the coefficients calculated using equations 15a and 15b), $\exp(-.7Q)/nC_p$, f/nC_p, and all of the products of fluxes and $1/nC_p$. Stepwise regression was used in the order of most significant to least significant variable and including only those variables with a 0.95 probability of significance. A total of 13 independent variables were considered. Table III gives the results.

Table III. Regression Coefficients for Theoretical Model of Weathering Steel Corrosion $C/t_w = \Sigma\beta_i P_i + \Sigma\alpha_i P_i/nC_p$

Variable	Units	Coefficient	Standard error	Partial F
C/t_w	μ/year	β_o=39.12		
TSP/nC_p		α_1=2292	175	171.10
f/nC_p		α_2=1573	262	36.05
$1/nC_p$		α_o=1381	308	20.15
NO_2 Flux	mg/cm^2 year	β_1=-8.85	1.85	22.88
SO_2 Flux	mg/cm^2 year	β_2=18.32	4.62	15.71
Rain Flux*	cm/year	β_3=-0.0798	0.0227	12.37
$EXP(-.7Q)/nC_p$		α_3=1104	335	10.85

* Rain Flux is expressed in cubic centimeters of rain per square centimeter of surface per year of wet time.

Variables are listed in the order in which they were entered into the regression. The resulting damage function ($C=(\Sigma\beta_i P_i+\Sigma\alpha_i P_i/nC_p)t_w$) can account for 95.65% of the variability.

Discussion of Results

The empirical damage function with coefficients calculated using equations 15a and 15b provides the best fit of the data (graphically presented in Figure 1). The gaseous pollutant fluxes are based on hourly concentrations and deposition velocities during periods of wetness. These do not differ dramatically from fluxes calculated from exposure period averages of deposition velocities and concentrations. The TSP fluxes are calculated from exposure period averages of deposition velocities and concentrations. The rain fluxes are the amounts of rain divided by times of wetness. Fraction of time when wet (f) is for a critical relative humidity of 85%. This equation can be used to predict weathering steel corrosion as a function of environmental conditions.

The coefficients in Table 3 provide a better theoretical understanding of how the different factors affect the corrosion of weathering steel. The β coefficients affect the solubility of the protective oxide layer and the α coefficients affect the diffusivity through the layer. The large ratio of α/β confirms the relative insolubility of the rust on weathering steel in most environments. Sulfur dioxide increases the solubility of the film while NO_2 and rain decrease the solubility. Rain apparently washes away acidic components (deposited during dew formation) that increase the solubility.

The α coefficient for TSP is highly significant. Accumulation of particles in the oxide layer appears to increase the diffusivity of ions or the electrical conductivity of the film. TSP does not appear to enhance the solubility of the film. Increasing the fraction of time-of-wetness appears to incrase the diffusivity through the layer. This could actually be a time function of a matter of hours. The diurnal cycle suggests that while the film is wet it becomes less protective with time; when it is dry it becomes

more protective with time. When f is large the film apparently is not dry long enough to reach a desired level of protectivity. The temperature effect is as expected; diffusion increases as temperature increases.

Conclusions

Weathering steel corrosion can be described as competing mechanisms of formation and dissolution of a protective oxide layer during periods of wetness.

Empirically, the best fit of the corrosion data suggests that time-of-wetness of the steel is best defined as the time when the dew point exceeds 0°C and the relative humidity exceeds 85% plus the time during rain when the relative humidity does not exceed 85%.

Three variables increase the diffusivity through the oxide film; 1) fraction of time when wet, 2) temperature, and 3) TSP flux.

Solubility of the oxide film is increased by increasing the flux of sulfur oxides during periods of wetness.

Dissolution of the oxide film is reduced by increasing the fluxes of oxides
of nitrogen and rain.

Ozone appears to have no significant effect on the corrosion of weathering steel.

Literature Cited

1. Schiermeier, F. A. Environmental Sci. Technol. 1978, 12, 644.
2. Mansfeld, F. "Regional Air Pollution Study: Effects of Airborne Sulfur Pollutants on Materials"; EPA-600/4-80-007, 1980.
3. Haynie, F. H.; Upham, J. B. Materials Protection and Performance 1971, 10, 18.
4. Mattsson, E. Materials Performance 1982, 21, 9.
5. Hern, D. H.; Taterka, M. H. "Regional Air Monitoring System Flow and Procedures Manual"; EPA Contract 68-02-2093, Rockwell International, Creve Coeur, Mo. 1977.
6. Haynie, F. H. Durability of Building Materials 1982/1983, 1, 241.
7. Knudson, J. G.; Katz, D. L. "Fluid Dynamics and Heat Transfer"; University of Michigan, Ann Arbor, Michigan, 1954, p. 38 and p. 149.

Figure 1. Fit of weathering steel corrosion data to At_w^n model, where A and n are functions of environmental parameters